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⑤④ **Pickling and tanning process and pickling composition.**

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Description

This invention relates to an improved pickling and tanning process and a pickling composition used therefor. More particularly it relates to a pickling and tanning process improved over a process disclosed in
 5 Japanese Patent Application 20517/78 (Japanese Patent Application Laying-Open Gazette 113401/79) filed by the same applicant as in the present application, the latter process comprising treating in a pickling bath incorporated with urotropin (hexamethylenetetramine) and then effecting chrome tanning in the same bath, and it also relates to a pickling composition used for the improved process.

The tanning process disclosed in said Gazette 113401/79 is characterized by adding to a pickling bath
 10 0.2—10 parts of urotropin per 100 parts of a hide (raw) and then effecting tanning with a chrome tanning agent in a less amount than usual in the presence or absence of a basicity adjuster such as sodium bicarbonate thereby to obtain satisfactory leathers (tanned) having substantially the same properties as conventional ones while greatly decreasing the chromium content in the waste effluent.

One of the hitherto known and widely used tanning processes comprises tanning with a chromium
 15 salt. As is widely known, the conventional chrome tanning process comprising pickling a hide which has been subjected to preliminary treatments (or beamhouse works) such as depilation, decalcification, beating and water washing, in a pickling bath containing an acid and a neutral salt and then adding a chromium tanning agent, a basicity adjuster and the like to the bath to tan the pickled hide therein. The main ingredient of the tanning solution usually used in this conventional tanning process is basic chromium
 20 sulphate expressed by $\text{Cr}(\text{OH})\text{SO}_4$.

If a depilated, decalcified, beaten and water washed hide is immersed in said chrome tanning solution, the chromium will precipitate in the texture of the hide to inhibit the reaction thereof with the collagen, the protein of the hide, thereby to lose the tanning effect since the hide is weakly alkaline. Thus, it is necessary
 25 to make the hide acidic by subjecting to a pickling treatment as a preliminary treatment prior to being tanned. In the pickling treatment, sulphuric acid or a mixed liquid of sulphuric acid and formic acid is usually employed.

Since a hide tends to swell even in an acidic bath, a neutral salt such as sodium chloride is usually added thereto to prevent the swelling in the step of pickling. In general, 100 parts by weight of a hide are
 30 incorporated with 30—100 parts by weight of water and with sodium chloride in such an amount that a pickling solution to be prepared exhibits 6—7° Bé in a drum, after which the drum is rotated. About 10 minutes after the start of rotation of the drum, sulphuric acid or a mixed aqueous solution thereof with formic acid is added in such an amount that the resulting pickling solution has a pH value of about 3. The pickling treatment is thus carried out for 3—24 hours.

The pickling treatment is carried out usually at 10—20°C since the temperature is restricted in view of
 35 the fact that the thermal shrinkage temperature for the hide is 35—40°C. If the pickling temperature is too high, that is, it rises near said thermal shrinkage temperature, the hide is abraded in the drum whereby the resulting tanned hide tends to create an abrasion on the surface and consequently degrade in quality.

The pickling solution or bath is incorporated with 5—10 (1.25—2.5 in terms of Cr_2O_3) parts by weight of
 40 a chrome tanning agent or a new bath containing the same tanning agent is prepared. The hide which has been pickled, is then immersed in the same bath incorporated with the tanning agent or in the new bath whereby the tannage thereof proceeds and the thermal shrinkage temperature therefor rises. In this case, the bath may be allowed to rise in temperature to about 40°C. During the tannage, an alkali agent such as sodium bicarbonate is usually added to the bath in order to raise the basicity of the chrome thereby
 45 increasing the reactivity thereof with the hide; in this case the sodium carbonate is added in aqueous solution and in portions, and the tannage is carried out for about 8 hours. The tanned hide is withdrawn from the bath at the point where the final pH value of the bath is 3.5—4.0 and the thermal shrinkage temperature for the hide reaches 77—120°C, or otherwise it is withdrawn from the bath after still leaving therein overnight. The tanned hide so withdrawn is aged at room temperature for 1—3 days, thereafter
 50 drained and then subjected to finishing treatments to obtain a product leather.

In the aforementioned tannage, the amount of chromium combined with the hide is usually 50—70%
 55 of the chrome tanning agent used while the remainder thereof becomes a tannage waste effluent. Since chromium is a heavy metal and the disposal thereof without further treatments raises problems as to environmental pollution, it is necessary to remove and recover the chromium from the tannage waste effluent. To this end, there are plants where such a tannage waste effluent is subjected to chemical treatments and the like to remove the chromium therefrom and allow the chromium-free effluent to flow outside.

The leather so obtained by chrome tanning is characterized by its thermal shrinkage temperature in the
 60 bath being 77—120°C and, thus, it has satisfactory heat resistance, putrefaction-resistance and chemical resistance as compared with that obtained by other types of tanning. It has a further advantage that it does not greatly change in textural structure as compared with a non-tanned hide. Particularly, it is excellent in flexibility and resilience as compared with a leather obtained by vegetable tanning.

The applicant previously filed Japanese Patent Application 20517/78 (Japanese Patent Application Laying-Open Gazette 113401/79 and EP—A—0014721) for a patent on a process for minimizing the
 65 chromium content in the tannage waste effluent without impairing the aforesaid features of a leather to be obtained by chrome tanning. However, this published process requires a time of one day or longer from the

start of pickling to the end of tanning, this being disadvantageous in operating an overall tanning equipment efficiently. If tannage is carried out in factories capable of operating tannage only once a day using the published process, the factories will require more of the equipment to produce the same amount of tanned hide (leather) as those capable of operating tannage using the same equipment more efficiently than the former or they will produce a less amount of product leather than the latter unless the tannage operation in the former can be operated more efficiently.

In addition, the temperature for the pickling treatment in said published process should preferably be in the range of 25—30°C to increase the effect obtained by the addition of urotropin and is higher than the temperature (10—20°C) for the pickling treatments in earlier conventional chrome tanning processes whereby the resulting leather disadvantageously tends to have abrasions caused by the mechanical friction between the hide and the drum during the rotation thereof. This tendency is particularly remarkable with a less fresh hide.

Finally, in SU—A—323444, there is disclosed a process wherein a hide is first pickled and thereafter the pickled hide is tanned with a chromium salt. In this process, urotropin is used. However, the urotropin is used to treat the hide after it has tanned rather than being used to treat the hide in the pickling step. The use of urotropin for chrome tanning a hide or for treating a tanned hide is also disclosed in SU—A—533636, SU—A—314797 and DE—C—879453.

The present inventors made intensive studies in attempts to overcome these disadvantages and, as the result of their studies, found the following novel pickling and tanning process.

According to the present invention, there is provided a pickling and tanning process comprising the step of pickling a hide which has previously been subjected to beamhouse works with a pickling composition comprising (a) sulphuric acid or a mixture thereof with formic acid, (b) a neutral salt and (c) water, and the step of subjecting the thus pickling hide to tanning, characterised in that the pickling step is carried out in the presence of urotropin and at least one pickling improver selected from a chromium salt and an aluminium salt in respective amounts by weight of 0.01—0.2 parts as Cr_2O_3 , and 0.1—2 parts as Al_2O_3 per 100 parts by weight of the hide.

The present invention also provides a pickling composition characterised in that it comprises urotropin and a pickling improver selected from a chromium salt and an aluminium salt in respective amounts by weight of 0.1—100 parts as Cr_2O_3 and 1—1000 parts as Al_2O_3 per 100 parts by weight of the urotropin.

The process of this invention may preferably comprise, in the pickling step, introducing into a rotatable drum (made of wood for example) 100 parts by weight of a weakly alkaline hide having been subjected to preliminary treatments such as depilation, decalcification and water washing, 20—100 parts by weight of water and 5—10 parts by weight of sodium chloride or sodium sulphate, rotating the thus charged drum for 5—20 minutes, introducing 0.5—3 parts by weight of sulphuric acid or a mixture thereof with formic acid, together with 5—30 parts by weight of water, into the drum, rotating the drum for 20 minutes to 2 hours, adding within this time period 0.2—10 parts by weight of urotropin and 0.001—2 parts by weight of at least one pickling improver to the drum, the urotropin and pickling improver being added at the same time or added separately at a time interval of 5 minutes to 2 hours for example, rotating the drum for 1—12 hours to infiltrate the urotropin and pickling improver into the hide and, if desired, slowly adding a diluted sulphuric acid in such an amount that the ratio of urotropin to the total of sulphuric acid amounts to 0.5—1.0 followed by further rotating the drum for 2—5 hours, thereafter, in the tanning step, adding 0—1.5 parts by weight of a tanning agent such as a chrome tanning agent (as Cr_2O_3), rotating the drum for 5—10 hours and, if desired, thereafter allowing the drum to stand overnight in order to tan the pickled hide, and then withdrawing the tanned hide from the drum for finishing treatment to obtain a leather, particularly a leather which will not degrade with the lapse of time.

As is apparent from the above process of the present invention, the amount of a chrome tanning agent used is smaller than that used in the conventional tanning processes. It is particularly noted that there are cases where no chromium salt is required as a tanning agent in the final tanning step when the pickling improver used along with urotropin is a chromium salt. The tanned hide (or leather) from the drum is preferably aged for 1—3 days.

The pickling improvers used herein are chromium salts and aluminium salts and they may be added alone or in combination in the pickling step.

An object of this invention is to provide a process for producing a leather by pickling a hide with a pickling composition comprising urotropin and at least one pickling improver selected from chromium salts and aluminium salts and then tanning the pickled hide in a shorter time using a smaller amount of a tanning composition.

Another object is to provide a pickling composition including urotropin and at least one pickling improver selected from said chromium and aluminium salts.

Another object is to provide a process for producing a leather, which will not degrade with the lapse of time, by pickling a hide with a pickling solution comprising urotropin and at least one pickling improver selected from chromium and aluminium salts.

In one aspect of this invention, a neutral salt and sulphuric acid are added at the initial stage of the pickling step and, prior to the lapse of about 2 hours after said addition, a small amount of a chromium salt and/or aluminum salt may be added simultaneously with, before or after, the addition of urotropin. It is possible and convenient in the pickling step to add the chromium salt and/or aluminum salt in the form of a

mixture thereof with the urotropin using this urotropin as a medium for mixing. Such a mixture or composition obtained by mixing 100 parts by weight of urotropin with 0.1—100 parts by weight of a chromium salt (as Cr_2O_3) and/or 1—1000 parts by weight of an aluminum salt (as Al_2O_3), is very useful for the purpose of this invention. Under the pickling action in the presence of at least one of these pickling
 5 improvers, the thermal shrinkage temperature of the hide may be maintained about 55°C or higher thereby permitting the pickling temperature to rise beyond 30°C ; this not only enables the hide to be slightly tanned on the surface and made resistant to friction caused by mechanical rotation but also promotes the tanning effect obtainable by the reaction of the urotropin with the hide. It has thus been found possible that the pickling time is shortened and the total time for the pickling and tanning is reduced to 12—20 hours. This
 10 invention, in one aspect, is based on this finding or discovery.

According to this invention, sulphuric acid is added at the initial stage of the pickling step, within about 2 hours after which 0.01—0.2, preferably 0.05—0.1, parts of a chromium salt (as Cr_2O_3) and 0.1—2, preferably 0.5—1.5, parts of an aluminum salt (as Al_2O_3), per 100 parts by weight of the hide, are added whereby the hide becomes so heat-resistant as to be resistant to a thermal shrinkage temperature of as
 15 high as 50°C or higher, not to speak of a thermal shrinkage temperature of about 35°C , and is strengthened in fibrous texture thus enabling it to be preferably pickled at a higher temperature of 25 — 35°C than generally possible heretofore. In addition, the hide treated with a pickling solution so prepared has an increased resistance to friction caused by the drum rotation and the like thereby making it possible to prevent the resulting tanned hide or leather from being damaged.

20 In the meantime, it should be noted that all parts are by weight through the specification.

The chromium salts used in the pickling step of this invention may include $\text{Cr}_2(\text{SO}_4)_3$, CrCl_3 and $\text{Cr}(\text{OH})\text{SO}_4$ which may also be used as a tanning agent; the aluminum salts used herein may include $\text{Al}_2(\text{SO}_4)_3$ and AlCl_3 .

The mechanism of functions of these inorganic salts is not clearly known but is considered to be that
 25 the salts facilitate the reaction of urotropin with the hide thereby shortening the time necessary for the thermal shrinkage temperature and the pH value respectively reaching a fixed value in the pickling step and consequently hastening the time for addition of the chrome tanning agent. Thus, the total time taken for the pickling and the tanning is greatly reduced. The practice of pickling in this manner will permit the chrome tanning agent to be used in a smaller amount (only up to 1.5, preferably 0.01—1.5, parts as Cr_2O_3 for
 30 example) than conventional in order to obtain a leather having the same quality as a conventional one.

More particularly, the addition of 0.2—10 parts of urotropin and 0.1—2 parts of an aluminum salt as Al_2O_3 , will permit a chrome tanning agent to be used in an amount of as small as 0.0025—1.5 parts as Cr_2O_3 , which the addition of 0.2—10 parts of urotropin and 0.01—0.15 parts of a chromium salt as Cr_2O_3 , will permit a chrome tanning agent to be used in an amount of as small as up to 0.5, preferably 0.01—1.5, parts.

35 In addition, any chrome tanning agent may be dispensed with and a separate tanning step may consequently be omitted in a case where the tanning may also be effected with a chromium salt added in the pickling step. In this case, it is also possible to add other tanning agents such as mineral, vegetable tanning and synthetic tanning agents in substitution for the chrome tanning agents.

The use of too much of the chromium salt or aluminum salt will give a less tanning effect thereby
 40 resulting in the production of a leather having poor resilience or having a chromium- or aluminum-precipitated skin structure at the worst, this meaning that tanning effects are hindered. On the other hand, the use of an unduly small amount of the said inorganic salt will result in lengthening the time from the start of pickling to the end of tanning and degrading the resulting leather due to abrasion produced thereon without exhibiting the effects otherwise obtainable by the practice of this invention. The unsatisfactory
 45 leathers so obtained will sometimes change with the lapse of time, that is, they will gradually degrade in quality; for example, there may be cases where the thermal shrinkage temperature of the unsatisfactory leathers may lower by about 10% when 3 months have passed since the production thereof.

The chromium and aluminium salt pickling improvers are hereinafter referred to as "inorganic pickling improvers".

50 The pickling compositions used herein may, of course, contain a tanning agent as desired.

According to this invention, it is possible to reduce the chromium content in the waste tanning solution effluent, shorten the time required for tanning and produce a leather having excellent quality and satisfactory resistance to degradation with the lapse of time.

This invention is applicable as a necessary pickling process not only to chrome tanning processes
 55 using urotropin but also to other chrome tanning processes and tanning processes using vegetable tannin, a synthetic tanning agent or the like.

This invention will be better understood by the following non-limitative Examples and Comparative Examples wherein all parts are by weight unless otherwise specified.

60 In the Examples and Comparative Examples, the amounts of reagents used are expressed in "part(s)" per 100 parts of a hide which has previously been decalcified and beaten, and the measurement of the respective times at which the reagents were added was started at the time of the addition of sodium chloride.

It should be noted that the terms "depilate" and "decalcify" used herein have the same meanings as
 65 "unhair" and "delime", respectively.

It should also be noted that the term "beamhouse works" used herein is intended to mean depilation (if necessary), decalcification, beating and the like to be effected on a hide in the tanning industry.

Example 1

5 Pickling step

Five sheets of steer hides, produced in North America, which had been subjected to beamhouse works (depilation, decalcification and beating in this case), were washed with 200 parts of water per 100 parts of the hide, drained for 5 minutes and found to weigh 7.5 Kg. This weight was hereinafter expressed in terms of 100 parts.

10 The thus drained hides (100 parts) were introduced into a test drum having a 1-m diameter and rotatable at a speed of 15 r.p.m. and incorporated with 20 parts of water and 6 parts of sodium chloride, after which the drum so charged was started to rotate. Ten minutes later the whole mass in the drum was incorporated with an aqueous solution of 2 parts of sulphuric acid in 20 parts of water, 25 minutes later incorporated with 2 parts of urotropin and 1 hour later incorporated with 0.3 parts of Beachrome-S
15 (Registered Trade Mark for a powdery chrome tanning agent containing 25% of Cr_2O_3 , produced by Nippon Denko Co., Ltd.) (0.075 parts as Cr_2O_3). Then, the drum continued to rotate for 11 hours. Table 1 shows the time from the addition of the sodium chloride to the end of this 11-hour rotation of the drum, the temperature of a bath used, the thermal shrinkage temperature (hereinafter referred to as "Ts") of the pickled hide in the bath, and the pH thereof.

20 Pickling step

Subsequently, 3 parts of Beachrome (0.75 parts as Cr_2O_3) were added to the drum which was then rotated for 8 hours. When this rotation ended, the temperature of the bath was 38°C. The hide so tanned was withdrawn from the drum and allowed to stand for two days at room temperature for aging.

25 After all, it was 20 hours from the time of start of pickling to the time of end of tanning.

In Table 2 are shown the Ts, resilience and degree of damage of the thus obtained leather as well as the pH of the bath, the amount of the unreacted Cr_2O_3 remaining therein and the time required from the start of pickling to the end of tanning.

30 Example 2

Pickling step

The procedure of Example 1 was followed as far as the aqueous solution of 2 parts of sulphuric acid in 20 parts of water was added. 25 minutes later the whole mass in the drum was incorporated with 2 parts of urotropin and 0.1 part of Beachrome-S (0.025 parts as Cr_2O_3), after which the drum continued to rotate for 3
35 hours. When this 3-hour rotation completed, the pH of the bath was 3.0 and the Ts of the treated hide 65°C.

Tanning step

3 hours and 25 minutes later 3.2 parts of Beachrome (0.8 parts as Cr_2O_3) were added to the drum, and
40 the drum continued its rotation for 9 hours (the temperature of the bath at the time of completion of this rotation being 38°C), after which an aqueous solution of 2.6 parts of ammonium bicarbonate in 15 parts of water was added in 3 one-third portions at a time interval of 60 minutes and the drum continued its rotation for further 30 minutes.

The tanned hide (or leather) was withdrawn from the drum and allowed to stand at room temperature
45 for 2 days for aging.

After all, it took a total of about 16 hours to carry out the pickling and tanning.

In Table 2 are indicated the quality of the thus obtained leather, the properties of the bath, the time required for tanning, and the like.

50 Example 3

Pickling step

The procedure of Example 1 was followed as far as the addition of the aqueous solution of 2 parts of sulphuric acid in 20 parts of water. 25 minutes later a composition comprising 2 parts of urotropin and 0.3 parts of Beachrome-S was added to the drum and the drum continued its rotation for 3 hours. In Table 1 are
55 shown the time required from the addition of the sodium chloride to the end of this 3-hour rotation, the temperature of the bath at this time, the Ts of the tanned hide and the pH of the bath.

Tanning step

Then, the procedure of tanning of Example 1 was followed. The results are shown in Table 2.

60 Example 4

The procedure of Example 3 was followed except that a composition comprising 2 parts of urotropin and 0.5 parts of Beachrome-S (0.125 parts as Cr_2O_3) was added to the drum in the pickling step and 2.8 parts of Beachrome-S (0.7 parts as Cr_2O_3), in place of 3.0 parts thereof, were added thereto in the tanning step.

65 The results are shown in Table 2.

Example 5

The procedure of Example 3 was followed except that a composition comprising 2 parts of urotropin and 3 parts of aluminum sulphate $[\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}]$ (0.45 parts as Al_2O_3) was added to the drum in the pickling step. The pH of the bath prior to the addition of Beachrome in the tanning step was 3.4 and the Ts 63°C. Table 2 shows the quality of the thus obtained leather, the properties of the bath, the time required for the tanning, and the like.

Example 6

Pickling step

The procedure of Example 1 was followed as far as the addition of the aqueous solution of 2 parts of sulphuric acid in 20 parts of water. 15 minutes later 0.354 parts of chromium sulphate $[\text{Cr}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}]$ (0.075 parts as Cr_2O_3) were added thereto and 25 minutes later 2 parts of urotropin were added thereto, after which the drum continued its rotation for 11 hours.

Tanning step

The following procedure of chrome tanning was the same as in Example 1. The results obtained were the same as those obtained in Example 1.

Example 7

The procedure of Example 1 was followed except that 0.156 parts of chromium chloride (CrCl_3) (0.075 parts as Cr_2O_3) were used in the substitution for the 0.3 parts of Beachrome-S in the pickling step. The results obtained were the same as those obtained in Example 1.

Example 8

The procedure of Example 5 was followed except that 1.178 parts of aluminum chloride (AlCl_3) (0.45 parts as Al_2O_3) and chromium sulphate $[\text{Cr}_2(\text{SO}_4)_3]$ (0.075 parts as Cr_2O_3) were substituted for the $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ and the Beachrome-S in the pickling step. The results obtained were the same as those obtained in Example 5.

Example 9

The procedure of Example 1 was followed except that 0.193 parts of chromium sulphate $[\text{Cr}_2(\text{SO}_4)_3]$ (0.075 parts as Cr_2O_3) and 0.771 parts of aluminium sulphate $[\text{Al}_2(\text{SO}_4)_3]$ (0.23 parts as Al_2O_3) were substituted for the 0.3 parts of Beachrome-S in the pickling step. The results obtained were the same as those obtained in Example 1.

Comparative Example 1

The procedure of Example 3 was followed except that 2 parts of urotropin and 0.7 parts of Beachrome-S (0.18 parts as Cr_2O_3) were used in substitution for the 2 parts of urotropin and 0.3 parts of Beachrome-S in the pickling step and 2.6 parts of Beachrome-S (0.65 parts as Cr_2O_3) were used in substitution for the 3 parts of Beachrome-S in the tanning step. The results obtained are shown in Table 2.

Comparative Example 2

The procedure of Example 1 was followed as far as the addition of urotropin, and the drum was rotated for 4 hours without the addition of a chromium salt or aluminium salt and allowed to stand overnight for further immersion of the treated hide therein in the pickling step. In Table 1 are shown the time required from the addition of the sodium chloride to the end of this 4-hour rotation, the temperature of the bath, the Ts of the treated hide and the pH thereof. Twenty-two (22) hours after the addition of sodium chloride, 3.3 parts of Beachrome-S (0.83 parts as Cr_2O_3) were added to the drum in the tanning step and the drum was rotated for 8 hours, after which the temperature of the bath was then 38°C.

The tanned hide was withdrawn from the drum and then allowed to stand at room temperature for 2 days. The results are shown in Table 2.

Comparative Example 3

In accordance with the conventional chrome tanning formulation, 100 parts of a decalcified hide were introduced into a drum and incorporated with 80 parts of water and 8 parts of sodium chloride, and the drum began to be rotated. Ten minutes later the whole mass in the drum was incorporated with 0.8 parts of sulphuric acid and 0.4 parts of formic acid in the pickling step, 3 hours later incorporated with 3.3 parts of Beachrome-S (0.83 parts as Cr_2O_3) and 5 hours later incorporated in four portions at a time interval of 30 minutes with an aqueous solution of 0.3 parts of sodium bicarbonate in 3 parts of water in the tanning step.

Eleven (11) hours after the addition of sodium chloride the rotation of the drum was stopped and, at this time, the temperature of the bath was 38°C. After allowing the treated hide to be immersed for 1 hour in the drum, the tanned hide was withdrawn therefrom and then aged for 2 days. The results are shown in Table 2.

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TABLE 1

5		Time required (hr)	Temp. of bath (°C)	Ts of tanned hide (leather) (°C)	Ph of bath	Ts after aging overnight (°C)
	Example 1	12	45	71	4	85
10	Example 3	3	35	65	3	85
	Comparative Example 2	22	30	56	4	70

15 Comparative Example 4

The procedure of Comparative Example 3 was followed except that 8 parts of Beachrome-S (2.00 parts as Cr_2O_3) were substituted for 3.3 parts of Beachrome-S (0.83 parts as Cr_2O_3) in the tanning step. The results are shown in Table 2.

20 In Table 2, the time required for tanning indicates the one beginning at the start of pickling and ending at the end of tanning. The symbol "○" indicates that the leathers obtained by the present process are equal in resilience and damage to those obtained by the conventional chrome tanning processes, while the symbol "×" indicates the inferiority of the former to the latter in the same respects as above.

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TABLE 2

	Time required for tanning (hr)	Ph at the end of tanning	Amount of unreacted Cr_2O_3 at the end of tanning in bath Cr_2O_3 g/100 ml	Tanned hide (leather) T_s ($^{\circ}\text{C}$)	Degree of damage	Resilience of tanned hide (leather)
Example 1	20	3.7	0.1	110	○	○
Example 2	16	5.5	0.0002	110	○	○
Example 3	11.5	3.7	0.1	111	○	○
Example 4	11.5	3.8	0.1	110	○	○
Example 5	11.5	3.7	0.2	107	○	○
Comp. Example 1	11.5	3.7	0.1	111	○	×
Comp. Example 2	46	3.8	0.1	110	×	○
Comp. Example 3	21	3.7	0.2	97	○	○
Comp. Example 4	21	3.7	0.8	109	○	○

Claims

1. A pickling and tanning process comprising the step of pickling a hide which has previously been subjected to beamhouse works with a pickling composition comprising (a) sulphuric acid or a mixture thereof with formic acid, (b) a neutral salt and (c) water, and the step of subjecting the thus pickling hide to tanning, characterised in that the pickling step is carried out in the presence of urotropin and at least one pickling improver selected from a chromium salt and an aluminium salt in respective amounts by weight of 0.01—0.2 parts as Cr_2O_3 and 0.1—2 parts as Al_2O_3 per 100 parts by weight of the hide.
2. A process according to claim 1, wherein the tanning is chrome tanning.
3. A process according to claim 2, wherein a chromium salt used in the chrome tanning step is a basic chromium salt, and is used in an amount by weight of up to 1.5 parts as Cr_2O_3 .
4. A process according to any of claims 1 to 3, wherein, in the pickling step, the urotropin is used in an amount by weight of 0.2—10 parts per 100 parts by weight of the hide.
5. A process according to any of claims 1 to 4, wherein the chromium salt used in the pickling step is $\text{Cr}(\text{OH})\text{SO}_4$, $\text{Cr}_2(\text{SO}_4)_3$ or CrCl_3 .
6. A process according to any of claims 1 to 4, wherein the aluminium salt used in the pickling step is $\text{Al}_2(\text{SO}_4)_3$ or AlCl_3 .
7. A pickling composition characterised in that it comprises urotropin and a pickling improver selected from a chromium salt and a aluminium salt in respective amounts by weight of 0.1—100 parts as Cr_2O_3 and 1—1000 parts as Al_2O_3 per 100 parts by weight of the urotropin.
8. A pickling composition according to claim 7, wherein the chromium salt is $\text{Cr}(\text{OH})\text{SO}_4$, $\text{Cr}_2(\text{SO}_4)_3$ or CrCl_3 .
9. A pickling composition according to claim 7, wherein the aluminium salt is $\text{Al}_2(\text{SO}_4)_3$ or AlCl_3 .

Patentansprüche

1. Pickel- und Gerbverfahren, umfassend die Stufe des Pickelns einer Haut, die vorher den Arbeiten im Stangenhaus bzw. Gerbvorbearbeitungen unterzogen worden ist, mit einer Pickelzusammensetzung, umfassend
 - (a) Schwefelsäure oder eine Mischung hiervon mit Ameisensäure,
 - (b) ein neutrales Salz und
 - (c) Wasser, sowie die Stufe des Gerbens der so gepickelten Haut,
 dadurch gekennzeichnet, daß die Pickelstufe in Gegenwart von Urotropin und mindestens einem Pickelverbesserer bzw. -hilfsmittel, gewählt aus einem Chromsalz und einem Aluminiumsalz in entsprechenden Gewichtsmengen von 0,01 bis 0,2 Teilen, als Cr_2O_3 , und 0,1 bis 2 Teilen, als Al_2O_3 , pro 100 Gewichtsteile der Haut, durchgeführt wird.
2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß als Gerbung eine Chromgerbung angewandt wird.
3. Verfahren nach Anspruch 2, dadurch gekennzeichnet, daß bei der Chromgerbungsstufe als Chromsalz ein basisches Chromsalz in einer Gewichtsmenge von bis zu 1,5 Teilen, als Cr_2O_3 , verwendet wird.
4. Verfahren nach einem der Ansprüche 1 bis 3, dadurch gekennzeichnet, daß bei der Pickelstufe das Urotropin in einer Gewichtsmenge von 0,2 bis 10 Teile pro 100 Gewichtsteile der Haut, verwendet wird.
5. Verfahren nach einem der Ansprüche 1 bis 4, dadurch gekennzeichnet, daß das in der Pickelstufe verwendete Chromsalz $\text{Cr}(\text{OH})\text{SO}_4$, $\text{Cr}_2(\text{SO}_4)_3$ oder CrCl_3 ist.
6. Verfahren nach einem der Ansprüche 1 bis 4, dadurch gekennzeichnet, daß das in der Pickelstufe verwendete Aluminiumsalz $\text{Al}_2(\text{SO}_4)_3$ oder AlCl_3 ist.
7. Pickelzusammensetzung, dadurch gekennzeichnet, daß sie Urotropin und ein Pickelhilfsmittel, gewählt aus einem Chromsalz und einem Aluminiumsalz in entsprechenden Gewichtsmengen von 0,1 bis 100 Teilen, als Cr_2O_3 und 1 bis 1 000 Teilen, als Al_2O_3 , pro 100 Gewichtsteile Urotropin, umfaßt.
8. Pickelzusammensetzung nach Anspruch 7, dadurch gekennzeichnet, daß das Chromsalz $\text{Cr}(\text{OH})\text{SO}_4$, $\text{Cr}_2(\text{SO}_4)_3$ oder CrCl_3 ist.
9. Pickelzusammensetzung nach Anspruch 7, dadurch gekennzeichnet, daß das Aluminiumsalz $\text{Al}_2(\text{SO}_4)_3$ oder AlCl_3 ist.

Revendications

1. Un procédé de mise en jusee et de tannage comprenant l'étape de mise en jusee d'une peau que l'on a préalablement soumis aux travaux sur chevalet avec une composition de jusee qui comprend:
 - a. — de l'acide sulfurique ou un mélange de celui-ci avec de l'acide formique;
 - b. — un sel neutre; et
 - c. — de l'eau;
 et l'étape de tannage de la peau ayant subi cette mise en jusee, caractérisé en ce que l'étape de mise en jusee est mise en oeuvre en présence d'urotropine et d'au moins un agent d'amélioration de jusee

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constitué d'un sel de chrome et d'un sel d'aluminium en quantités respectives en poids de 0,01 à 0,2 partie de Cr_2O_3 et 0,1 à 2 parties de Al_2O_3 pour 100 parties en poids de la peau.

2. Un procédé selon la revendication 1, dans lequel le tannage est un tannage au chrome.

3. Un procédé selon la revendication 2, dans lequel le sel de chrome utilisé dans l'étape de tannage au chrome est un sel de chrome basique et il est utilisé en quantités pondérales allant jusqu'à 1,5 partie de Cr_2O_3 .

4. Un procédé selon l'une quelconque des revendications 1 à 3, dans lequel, dans l'étape de mise en jusée, on utilise l'urotropine en quantités de 0,2 à 10 parties en poids pour 100 parties de la peau.

5. Un procédé selon l'une quelconque des revendications 1 à 4, dans lequel le sel de chrome utilisé dans l'étape de mise en jusée est le $\text{Cr}(\text{OH})\text{SO}_4$, $\text{Cr}_2(\text{SO}_4)_3$ ou CrCl_3 .

6. Un procédé selon l'une quelconque des revendications 1 à 4, dans lequel le sel d'aluminium utilisé dans l'étape de mise en jusée est le $\text{Al}_2(\text{SO}_4)_3$ ou AlCl_3 .

7. Une composition de jusée caractérisée en ce qu'elle comprend de l'urotropine et un agent d'amélioration de jusée, constituée d'un sel de chrome et d'un sel d'aluminium en quantités pondérales respectives de 0,1 à 100 parties de Cr_2O_3 et de 1 à 1.000 parties de Al_2O_3 pour 100 parties en poids d'urotropine.

8. Une composition de jusée selon la revendication 7, dans laquelle le chrome est le $\text{Cr}(\text{OH})\text{SO}_4$, le $\text{Cr}_2(\text{SO}_4)_3$ ou le CrCl_3 .

9. Une composition de jusée selon la revendication 7, dans laquelle le sel d'aluminium est le $\text{Al}_2(\text{SO}_4)_3$ ou le AlCl_3 .

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